Heteroatom Chemistry
Volume 7, Number 1, 1996

Reaction of 2,4-Di-*t*-butyl-6-methylphenylphosphonous Dichloride with Chloroform in the Presence of Lithium Diisopropylamide

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Received 4 April 1995; revised 3 June 1995

ABSTRACT

2,4-Di-t-butyl-6-methylphenylphosphonous dichloride reacted with chloroform in the presence of lithium diisopropylamide to give (2,4-di-t-butyl-6-methylphenyl)(dichloromethyl)(1,2,2-trichloroethenyl)phosphine. The structure of this phosphine was analyzed by X-ray crystallography. This phosphine further reacted with butyllithium to give (1-butylpentylidene)(2,4-di-t-butyl-6-methylphenyl)phosphine bearing a low-coordinated phosphorus atom. © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

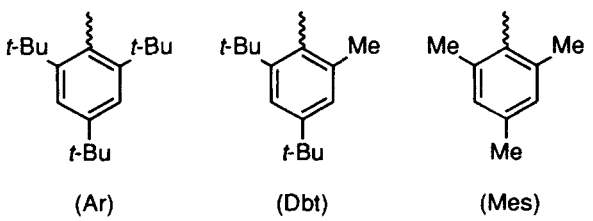
Utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl (abbreviated to Ar) group as a sterically protecting group, we have prepared various kinds of low-coordinated phosphorus compounds, such as diphosphenes [1], methylenephosphines [2], and phosphaallenes [3]. We have also been interested in protecting groups that are less bulky than the Ar group. Thus, the 2,4-di-*t*-butyl-6-methylphenyl (hereafter abbreviated to Dbt) and the mesityl (abbreviated to Mes) groups turned out to be useful to stabilize kinetically some unsymmetrical diphosphenes [4] carrying the Ar group and the Dbt or Mes group (Scheme 1).

We report here that 2,4-di-*t*-butyl-6-methylphenylphosphonous dichloride (**1**) showed different reactivities from the corresponding Ar derivatives toward chloroform/lithium diisopropylamide (LDA), giving unusual products.

RESULTS AND DISCUSSION

2,4-Di-t-butyl-6-methylphenylphosphonous Dichloride (1)

Phosphonous dichloride **1** [4] was prepared according to the conventional method starting from the corresponding bromobenzene. Thus, $DbtPCl_2$ (**1**) was obtained almost quantitatively when a bromine-metal exchange reaction with butyllithium was employed as shown in Scheme 2, while Baudler and



SCHEME 1

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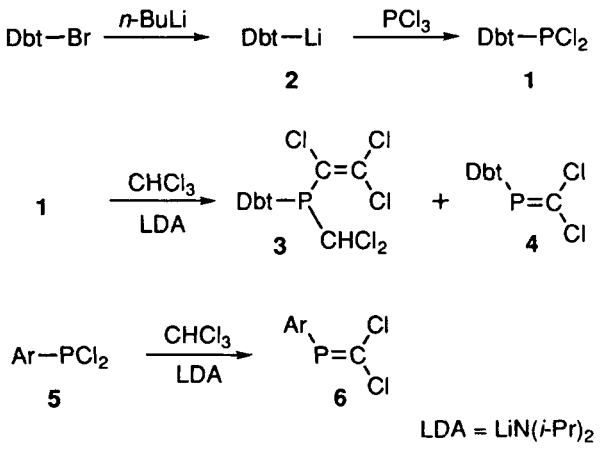


SCHEME 2

Simon [5] reported that a Grignard-type reagent, DbtMgBr, reacted with PCl_3 to give a mixture of $DbtPCl_2$, DbtPBrCl, and $DbtPBr_2$ in a ratio of 58:38:4.

The Reaction of 1 *with Chloroform in the Presence of Lithium Diisopropylamide*

When 1 was allowed to react with 2 molar equiv. of chloroform in the presence of 3 molar equiv. of LDA, (2,4-di-*t*-butyl-6-methylphenyl)(dichloromethyl)(1,2,2-trichloroethenyl)phosphine (3) was obtained as a major product in 25% yield, together with (2,4-di-*t*-butyl-6-methylphenyl)(dichloromethylene)phosphine (4) in 1% yield [6]. When 1 molar equiv. of chloroform and 2 molar equiv. of LDA were used during the reaction, 3 was obtained in 5% yield, together with 4 in 13% yield.

It should be noted that the reaction of 2,4,6-tri-*t*-butylphenylphosphonous dichloride (5) with chloroform/LDA gave (dichloromethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (6) in 83% yield under similar reaction conditions to those employed for 1 [7], but the corresponding trichloroethenylphosphine was not formed. The reaction of 1 or 5 with chloroform/LDA might be initiated by a nucleophilic displacement of one of the chlorine atoms of the phosphonous dichloride by the trichloromethyl group, as shown in Scheme 3. In the case of the reaction of 1, the intermediate $DbtP(Cl)(CCl_3)$ suffers from the second attack of $^-CCl_3$ onto the phosphorus atom leading to the formation of 3, while the bulky Ar group seems to protect $ArP(Cl)(CCl_3)$ from the attack of $^-CCl_3$. Under the reaction conditions, including a combination of chloroform and a strong base such as LDA, dichlorocarbene as a reactive intermediate might be formed and involved in producing polychloro-substituted products, 3 and 4, as well as 6. An electron-transfer process [8] or a halogen-metal exchange process [9] should be involved during the reaction to form a double bond [10], but there is no supporting evidence for an operating mechanism.

X-ray Analysis of (2,4-Di-t-butyl-6-methylphenyl)(dichloromethyl)(1,2,2-trichloroethenyl)phosphine (3)

The structure of 3 was confirmed by X-ray analysis. Figure 1 depicts the molecular structure for 3. Some important bond lengths and angles are listed in Table 1. Since the *p*-*t*-butyl group is disordered, the *R* factors are not sufficient enough to discuss the structural parameters in detail, but it is clear that 3 is a typical tertiary phosphine bearing aromatic, vinylic, and alkyl substituents. The atoms C(8), C(9), Cl(3), Cl(4), Cl(5) are coplanar within 0.038 Å where P(1) is located 0.155 Å off the plane. The Dbt aromatic ring [C(1)–C(6)] is almost planar within 0.03 Å, making an internal angle of 78° with the trichloroethenyl plane.

Reaction of 3 *with Butyllithium*

The reaction of 3 with butyllithium resulted in an unexpected formation of (1-butylpentylidene)(2,4-di-*t*-butyl-6-methylphenyl)phosphine (7) carrying a phosphorus atom in a low coordination state. Butyllithium appeared to have reacted with 3 as a nucleophile and a base. Thus, the formation of 7 is explainable by double nucleophilic attack of butyllithium on the dichloromethyl group, followed by deprotonation and elimination of dichloroacetylene [11] as shown in Scheme 4. An attempt to detect dichloroacetylene, however, was not successful.

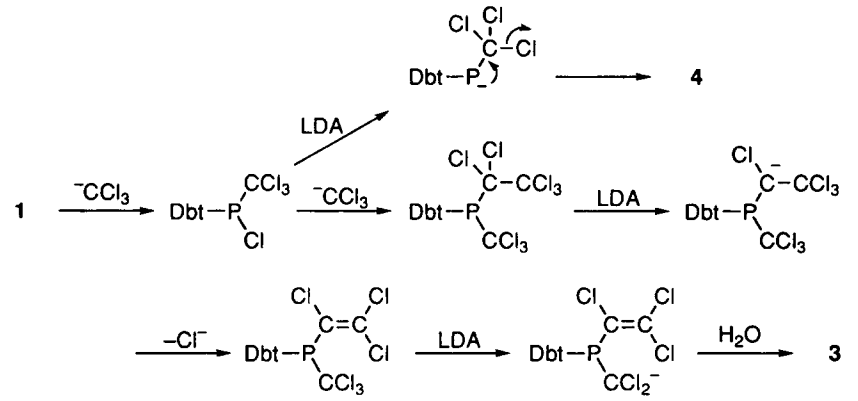
In summary, the presence of the Dbt group provides unusual reaction products in the reaction of $DbtPCl_2$ with chloroform in the presence of LDA. These results form a sharp contrast to those with the Ar group present, probably due to the less steric bulk around the phosphorus atom.

EXPERIMENTAL

Instruments

Melting points were determined with a Yanagimoto micro melting-point apparatus MP-J3 and are not corrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200P or AM600 spectrometer. ^{31}P NMR spectra were obtained with a Bruker AC200P spectrometer. Mass spectra were recorded on a JEOL HX-110, DX-303, AX-500, or a Hitachi M-2500S spectrometer. IR spectra were taken on a Horiba FT-300 spectrometer. X-ray diffraction data were

SCHEME 3



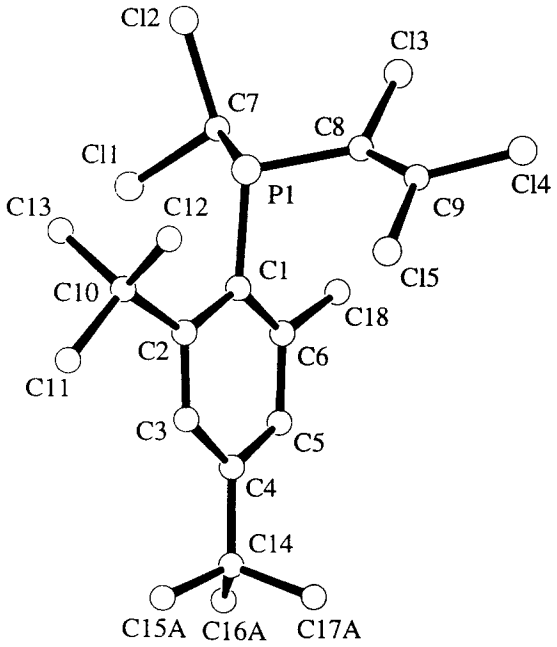
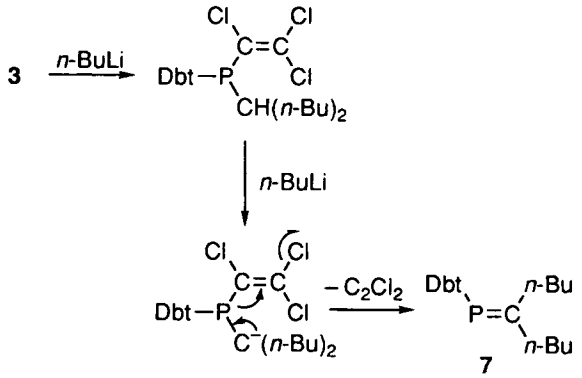


FIGURE 1 Molecular structure for **3** with atom labeling scheme. The *p*-*t*-butyl group (C15–C17) is disordered and the atoms with the predominant occupancy factor (0.55) are shown for clarity.

TABLE 1 Some Important Bond Lengths and Angles of **3**[a]

Bond length (Å)		*Bond angle* (°)	
P(1)–C(1)	1.855(8)	C(1)–P(1)–C(7)	103.5(3)
P(1)–C(7)	1.877(9)	C(1)–P(1)–C(8)	104.1(4)
P(1)–C(8)	1.842(10)	C(7)–P(1)–C(8)	98.3(4)
C(8)–C(9)	1.33(1)	P(1)–C(7)–Cl(1)	110.7(4)
C(7)–Cl(1)	1.784(9)	P(1)–C(7)–Cl(2)	107.6(4)
C(7)–Cl(2)	1.790(8)	P(1)–C(8)–Cl(3)	119.3(6)
C(8)–Cl(3)	1.715(8)	P(1)–C(8)–C(9)	124.7(7)
C(9)–Cl(4)	1.70(1)	Cl(3)–C(8)–C(9)	115.3(7)
C(9)–Cl(5)	1.74(1)	C(8)–C(9)–Cl(4)	127.3(8)
C(6)–C(18)	1.51(1)	C(8)–C(9)–Cl(5)	120.7(8)
		Cl(4)–C(9)–Cl(5)	112.0(6)

[a]Numbers in parentheses are estimated standard deviations.



SCHEME 4

collected on a Rigaku AFC-7S four-circle diffractometer.

2,4-Di-t-butyl-6-methylphenylphosphonous Dichloride (1)

To a solution of 2-bromo-1,5-di-*t*-butyl-3-methylbenzene (0.900 g, 3.18 mmol) [12,13] in THF (25 mL) butyllithium was added (4.3 mmol, hexane solution) at −78°C and stirred for 10 minutes under an argon atmosphere. Phosphorus trichloride (0.70 mL, 8.0 mmol) was added to the mixture and stirred for 10 minutes. The reaction mixture was gradually warmed to room temperature and finally refluxed for 1.5 hours. The mixture was then cooled to room temperature, concentrated in vacuo, extracted with pentane, washed with aq $NaHCO_3$, and dried over $MgSO_4$. Evaporation of the solvent afforded 0.94 g of 1 (97% yield based on the starting bromobenzene). 1: Colorless crystals, mp 100°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.31 (9H, s, *p*-*t*-Bu), 1.58 (9H, d, $^5J_{PH}$ = 0.8 Hz, *o*-*t*-Bu), 2.91 (3H, d, $^4J_{PH}$ = 0.5 Hz, *o*-Me), 7.19 (1H, dd, $^4J_{HH}$ = 2.5 Hz and $^4J_{PH}$ = 1.0 Hz, 5-Dbt), and 7.33 (1H, dd, $^4J_{HH}$ = 2.5 Hz and $^4J_{PH}$ = 6.7 Hz, 3-Dbt); ^{31}P[^{1}H] NMR (81 MHz, $CDCl_3$) δ = 167.9.

Reaction of 1 *with Chloroform in the Presence of Lithium Diisopropylamide*

To a solution of 1 (0.94 g, 2.8 mmol) and chloroform (0.48 mL, 6.0 mmol) in THF (25 mL) was added LDA (9.28 mmol, prepared from diisopropylamine and butyllithium in 10 mL of THF at 0°C) at −120°C over a 10 minute period. The reaction mixture was stirred for 30 minutes and warmed to room temperature. The solvent was evaporated in vacuo to give, after silica-gel column chromatography, 0.34 g (25%) of (2,4-di-*t*-butyl-6-methylphenyl)(dichloromethyl)-(1,2,2-trichloroethenyl)phosphine (3) together with 5.0 mg of (2,4-di-*t*-butyl-6-methylphenyl)(dichloromethylene)phosphine (4) in 1% yield based on the phosphine 1 used. When 1 (0.67 g, 2.2 mmol) was allowed to react with chloroform (2.3 mmol) in the presence of LDA (4.3 mmol) at −78°C, 4 (88 mg, 13% yield based on 1 consumed) was obtained together with 3 (50 mg, 5% yield). 3: Pale yellow crystals, mp 85–87°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.30 (9H, s, *p*-*t*-Bu), 1.68 (9H, d, $^5J_{PH}$ = 0.5 Hz, *o*-*t*-Bu), 2.35 (3H, d, $^4J_{PH}$ = 0.5 Hz, *o*-Me), 6.79 (1H, d, $^2J_{PH}$ = 1.7 Hz, $CHCl_2$), 7.07 (1H, dd, $^4J_{PH}$ = 0.5 Hz and $^4J_{HH}$ = 1.8 Hz, 5-Dbt), and 7.43 (1H, dd, $^4J_{PH}$ = 6.0 Hz and $^4J_{HH}$ = 1.8 Hz, 3-Dbt); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 24.1 (s, *o*-Me), 31.1 (s, *p*-CMe_3), 34.2 (d, $^4J_{PC}$ = 14.2 Hz, *o*-CMe_3), 34.9 (d, $^5J_{PC}$ = 1.0 Hz, *p*-CMe_3), 38.2 (d, $^3J_{PC}$ = 2.9 Hz, *o*-CMe_3), 69.2 (d, $^1J_{PC}$ = 46.0 Hz, $CHCl_2$), 122.4 (d, $^3J_{PC}$ = 12.2 Hz, 3-Dbt), 123.3 (d, $^1J_{PC}$ = 33.1 Hz, CCl = CCl_2), 126.4 (d, $^2J_{PC}$ = 37.2 Hz, CCl = CCl_2), 126.5 (d, $^3J_{PC}$ = 1.0 Hz, 5-Dbt), 128.5 (d, $^1J_{PC}$ = 69.1 Hz, 1-Dbt), 143.9 (d, $^4J_{PC}$ = 1.0 Hz, 4-Dbt), 154.1 (d, $^2J_{PC}$ = 1.0 Hz, 6-Dbt), and 157.6 (d, $^2J_{PC}$ = 32.6 Hz, 2-Dbt); ^{31}P NMR (81 MHz, $CDCl_3$) δ = 23.0 (d, $^4J_{PH}$ = 6.0 Hz); IR (KBr) 2950, 2906, and 1595 cm^{-1}; MS (70 eV, EI) *m/z* (rel intensity) 450 (M^++4; 4), 448 (M^++2; 7), 446 (M^+; 5), 417 (M^+–Cl+6; 15), 415 (M^+–Cl+4; 30), 413 (M^+–Cl+2; 58), 411 (M^+–Cl; 47), 367 (M^+–$CHCl_2$+4; 20), 365 (M^+–$CHCl_2$+2; 56), 363 (M^+–$CHCl_2$; 57), 329 (M^+–$CHCl_2$–Cl+1; 7), 327 (M^+–$CHCl_2$–Cl–1; 12), and 57 (t-Bu^+; 100). Found: *m/z* 446.0098. Calcd for $C_{18}H_{24}{}^{35}Cl_5P$: M, 446.0058. 4: Colorless crystals, mp 65–70°C (lit, 71–72°C [5]); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.32 (9H, s, *p*-*t*-Bu), 1.52 (9H, d, $^5J_{PH}$ = 0.5 Hz, *o*-*t*-Bu), 2.45 (3H, d, $^4J_{PH}$ = 0.5 Hz, *o*-Me), 7.14 (1H, dd, $^4J_{HH}$ = 2.0 Hz and $^4J_{PH}$ = 0.5 Hz, 5-Dbt), and 7.38 (dd, $^4J_{HH}$ = 2.0 Hz and $^4J_{PH}$ = 2.0 Hz, 3-Dbt); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 235.1.

Reaction of 3 *with Butyllithium*

Butyllithium (4.3 mmol) was added to a solution of 3 (75.2 mg, 0.168 mmol) in ether (11 mL) at −78°C to give a deep red solution. After being stirred for 30 minutes, the reaction mixture was warmed to room temperature. The solvent was evaporated to give 7.2 mg (12%) of (1-butylpentylidene)(2,4-di-*t*-butyl-6-methylphenyl)phosphine (7) after silica-gel column chromatography. Other products were not identified. 7: Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.72 (3H, t, $^3J_{HH}$ = 6.9 Hz, *Z*-CH_2CH_3), 0.96 (3H, t, $^3J_{HH}$ = 6.9 Hz, *E*-CH_2CH_3), 1.10 (2H, qt, $^3J_{HH}$ = 6.9 Hz and $^3J_{HH}$ = 7.2 Hz, *Z*-CH_2CH_3), 1.26 (2H, tt, $^3J_{HH}$ = 7.2 Hz and $^3J_{HH}$ = 7.8 Hz, *Z*-$CH_2CH_2CH_3$), 1.32 (9H, s, *p*-*t*-Bu), 1.42 (2H, qt, $^3J_{HH}$ = 6.9 Hz and $^3J_{HH}$ = 7.2 Hz, *E*-CH_2CH_3), 1.45 (9H, brs, *o*-*t*-Bu), 1.51 (3H, tt, $^3J_{HH}$ = 7.2 Hz and $^3J_{HH}$ = 7.8 Hz, *E*-$CH_2CH_2CH_3$), 2.07 (2H, dt, $^3J_{PH}$ = 11.0 Hz and $^3J_{HH}$ = 7.8 Hz, *Z*-$CH_2CH_2CH_2CH_3$), 2.32 (3H, brs, Me), 2.52 (2H, m, $^3J_{PH}$ = 21.9 Hz, $^3J_{HH}$ = 7.8 Hz, and $^4J_{HH}$ = 3.0 Hz, *E*-$CH_2CH_2CH_2CH_3$), 7.06 (1H, m, 5-Dbt), and 7.32 (1H, m, 3-Dbt); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 13.7 (s, *Z*-CH_2CH_3), 14.0 (s, *E*-CH_2CH_3), 22.6 (s, *E*-CH_2CH_3), 22.8 (s, *Z*-CH_2CH_3), 24.3 (d, $^3J_{PC}$ = 9.0 Hz, *o*-Me), 29.0 (d, $^3J_{PC}$ = 7.4 Hz, *E*-$CH_2CH_2CH_3$), 31.3 (s, *p*-CMe_3), 31.6 (s, *Z*-$CH_2CH_2CH_3$), 31.6 (d, $^4J_{PC}$ = 6.6 Hz, *o*-CMe_3), 34.6 (s, *p*-CMe_3), 35.9 (d, $^2J_{PC}$ = 15.9 Hz, *Z*-$CH_2CH_2CH_2CH_3$), 37.3 (s, *o*-CMe_3), 37.9 (d, $^2J_{PC}$ = 40.3 Hz, *E*-$CH_2CH_2CH_2CH_3$), 120.8 (s, 3-Dbt), 125.0 (s, 5-Dbt), 136.0 (d, $^1J_{PC}$ = 52.4 Hz, 1-Dbt), 140.7 (d, $^2J_{PC}$ = 3.3 Hz, 6-Dbt), 150.4 (s, 4-Dbt), 152.9 (d, $^2J_{PC}$ = 4.3 Hz, 2-Dbt), and 193.6 (d, $^1J_{PC}$ = 41.4 Hz, P = C); ^{31}P NMR (81 MHz, $CDCl_3$) δ = 219.9 (tt, $^3J_{PH}$ = 11.0 and 21.9 Hz); IR (neat) 2960 and 1594 cm^{-1}; MS (70 eV, EI) *m/z* (rel intensity) 360 (M^+; 20), 317 (M^+–C_3H_7; 100), 303 (M^+–Bu; 10), 234 (DbtP$^+$; 26), and 57 (Bu^+; 58). Found: *m/z* 360.2949. Calcd for $C_{24}H_{41}P$: M, 360.2946.

X-ray Crystallographic Analysis of 3

The compound 3 was recrystallized from chloroform to give pale yellow prisms. $C_{18}H_{24}Cl_5P$, molecular weight, 448.63. Crystal data: monoclinic, space group $P2_1/c$, a = 9.104(5) Å, b = 9.825(4) Å, c = 24.503(3) Å, β = 90.90(2)°, V = 2191(1) Å^3; Z = 4; ρ = 1.360 g cm^{-3}, μ = 7.33 cm^{-1}. Diffracted intensities were recorded at 296 K on a Rigaku AFC-7S diffractometer (ω-2θ scan, $2\theta_{max}$ = 50.0°, Mo$K\alpha$), graphite monochromated. Number of reflections measured, total 4377, unique 4101; Number of observations [$I > 3.00\sigma(I)$], 2811. An empirical absorption correction using the program DIFABS [14] was applied. The structure was solved by a direct method SHELXS86 [15] and expanded using Fourier techniques (DIRDIF92) [16]. The structure was refined by a full-matrix least-squares refinement. The *p*-*t*-butyl group was disordered with refined occupancy factors of 0.55 and 0.45. The nonhydrogen atoms were

refined anisotropically except for the disordered carbon atoms (C15–C17). Hydrogen atoms except those on the *p*-*t*-butyl group were included but not refined. The R factor and R_w factor were 0.093 and 0.145, respectively. All calculations were performed using the TEXSAN [17] crystallographic software package of Molecular Structure Corporation.

ACKNOWLEDGMENTS

This work was supported in part by the Grants-in-Aid for Scientific Research (Nos. 02403008 and 06453033) from the Ministry of Education, Science, Sports, and Culture, Japanese Government. The authors also thank Tosoh Akzo Co., Ltd. for donation of organolithium reagents.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, torsion angles, and structure factors for compound **3** (25 pages) are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, United Kingdom.

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[7] To a solution of **5** (0.55 g, 1.7 mmol) and chloroform (0.28 mL, 3.5 mmol) in THF (15 mL) was added LDA (5.1 mmol, prepared from diisopropylamine and butyllithium in 5 mL of THF at 0°C) at −120°C over a 5 minute period. The reaction mixture was stirred for 30 minutes and warmed to room temperature. The solvent was evaporated in vacuo to give 0.50 g (83% yield) of **6** after column-chromatographic treatment. See also S. J. Goede, F. Bickelhaupt, *Chem. Ber., 124,* 1991, 2677.
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